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Methods For Cleaning Semiconductor Surfaces

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TECHNICAL FIELD

This invention pertains to methods for cleaning surfaces of semiconductor articles, and more particularly to methods for cleaning silicon containing surfaces, such as on silicon semiconductor wafers.

BACKGROUND OF THE INVENTION

The production of semiconductors into various types of integrated circuits, displays, memories, sensors and other devices typically requires cleaning of semiconductor surfaces to remove contaminants. In many cases the presence of even small amounts of contamination on a semiconductor surface will impair or destroy operation of devices formed from the contaminated semiconductor material.

A common semiconductor material used for production of semiconductor devices is silicon, which is most typically in the form of a silicon containing wafer. The so-called "RCA clean" has been the standard clean sequence utilized by the industry for cleaning silicon wafers for the past two decades. An RCA clean process is illustrated in Fig. 1, and comprises steps 1A-II.

Referring to step 1A, one or more silicon-comprising semiconductor wafers are subjected to a so-called "piranha" cleaning step. The piranha cleaning step typically comprises dipping the wafers in an inorganic oxidant, such as a solution containing sulfuric acid and hydrogen peroxide. This step is intended to remove organic material from a surface of the semiconductor article. A typical piranha cleaning solution would comprise

1 hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) in a ratio of about
2 1:5 to about 1:50 (hydrogen peroxide: H_2SO_4).

3 Referring to step 1B, the wafers are rinsed with deionized water.
4 The deionized water rinse typically occurs at room temperatures, commonly
5 from about 18°C to about 23°C. Preferably, the rinse utilizes water with
6 a high resistivity, such as from about 10 megohms-centimeter to about 18
7 megohms-centimeter.

8 Referring to step 1C, the wafers are subjected to a so-called "HF
9 clean". The HF clean is typically used to remove an oxide film from the
10 surfaces of the semiconductor wafers. Such oxide film may be formed,
11 for example, during the above-discussed piranha clean or due to exposure
12 of the semiconductor wafer or other article to air or other sources of
13 oxygen. The HF clean typically involves dipping the wafers in a solution
14 of water and hydrofluoric acid, with the water:hydrogen fluoride ratio
15 commonly being in the range of from approximately 1000:1 to
16 approximately 100:1.

17 Referring to step 1D, the semiconductor wafers are rinsed with
18 deionized water to remove hydrogen fluoride and various materials loosened
19 from the surface of the wafer.

20 Referring to step 1E, the wafers are subjected to a so-called
21 "Standard Clean 1" step, commonly referred to as an "SC1" step. The
22 SC1 step is principally directed to removing various particulate materials
23 from the semiconductor surfaces which can more easily attach as a result
24 of the surface being made hydrophobic by the hydrogen fluoride cleaning

1 step explained above, step 1C. In a typical SC1 step, the wafers are
2 submerged in a solution of water, hydrogen peroxide and ammonium
3 hydroxide (for example 5:1:1 by volume), at temperatures from about 75°C
4 to about 80°C for a time of from about 2 minutes to about 15 minutes.

5 Referring to step 1F, the wafers are subjected to a deionized water
6 rinse to remove the above-described SC1 solution from the wafers.
7 Typically, this rinse, like the rinse in step 1D, is relatively short to
8 minimize regrowth of oxide on the wafers.

9 Referring to step 1G, the wafers are subjected to a so-called
10 "Standard Clean 2" step, commonly referred to as an "SC2" step. The
11 SC2 step is thought to desorb atomic and ionic contaminants from the
12 wafers. In particular, the SC2 step is intended to remove metals
13 deposited on the wafer surface during the HF cleaning step and SC1 step.
14 In a typical SC2 step, the wafers are submerged in a solution of
15 H₂O:HCl:H₂O₂ (for example 6:1:1 by volume). The SC2 step can be
16 carried out at temperatures which are elevated above common room
17 temperatures. Examples of elevated temperatures sometimes used are from
18 about 75°C to about 80°C. The SC2 step can be effected for various
19 times, for example for times from about 1 to about 10 minutes.

20 Referring to step 1H, the wafers are subjected to a deionized water
21 rinse, similar to the rinse described above regarding step 1D, to remove
22 the above-described SC2 solution from the wafers.

23 Referring to step 1I, the wafers are subjected to a drying step.
24 The drying step can be done using a variety of processes. Standard

1 processes can include relatively more sophisticated isopropyl alcohol drying
2 systems, spin rinse driers, and other drying technologies. One standard
3 drying procedure employs a combined rinse and dry which involves: 1)
4 loading a cassette of wafers into a rinse tank; 2) spraying the cassette
5 with rinse water until the water reaches a predetermined level; and 3)
6 quickly dumping the water. After several rinse/dump cycles, the wafers
7 are typically dried by exposure to a heated nitrogen gas.

8 The above-described RCA clean has the disadvantage of requiring
9 numerous discrete steps for wafer cleaning. This necessarily increases both
10 equipment costs, costs of processing facility space, and costs for added
11 labor and processing time to complete numerous processing steps. It has
12 long been recognized that a standard cleaning process is needed for
13 semiconductor articles which can provide both fewer discrete steps and the
14 exceedingly high degree of cleanliness needed in the semiconductor
15 processing industry.

16 The RCA clean also has the further disadvantage of requiring four
17 distinct chemical based cleaning steps (steps 1A, 1C, 1F and 1H), each
18 of which requires a different chemical bath solution. Accordingly, many
19 types of equipment designed to perform the RCA clean require four
20 distinct tanks of cleaning solutions: a tank for the piranha mixture, a tank
21 for the hydrogen fluoride mixture, a tank for the SC1 mixture, and a tank
22 for the SC2 mixture. This renders the equipment more expensive and
23 bulky. There is also an ancillary requirement to dispose of spent
24 chemicals. When more chemicals are used then there is associated

1 increases in chemical disposal costs. Accordingly, it is long been
2 recognized as strongly desirable to have improved cleaning processes which
3 reduce the number and volume of chemicals needed to clean semiconductor
4 articles.

5 6 BRIEF DESCRIPTION OF THE DRAWINGS

7 Preferred embodiments of the invention are described below with
8 reference to the following accompanying drawings.

9 Fig. 1 is a block diagram of a prior art semiconductor wafer
10 cleaning process.

11 Fig. 2 is a block diagram of a first embodiment cleaning process
12 of the present invention.

13 Fig. 3 is a block diagram of an alternative embodiment cleaning
14 process according to aspects of the present invention.

15 16 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

17 This disclosure of the invention is submitted in furtherance of the
18 constitutional purposes of the U.S. Patent Laws "to promote the progress
19 of science and useful arts" (Article 1, Section 8).

20 The invention pertains to methods for cleaning surfaces of wafers
21 and other semiconductor articles. The surfaces being cleaned can be made
22 from a variety of semiconductor materials and formulations. The specific
23 preferred processes described herein are most appropriately used in cleaning
24

1 semiconductor surfaces which are principally or wholly silicon
2 semiconductor surfaces.

3 The invention in part resides in or stems from a recognition that
4 a significant amount of the contamination removed by the prior art RCA
5 clean SC1 and SC2 steps (the above-described steps 1E and 1G) commonly
6 originates as contamination in the upstream solutions of the RCA clean
7 process. For instance, a significant amount of the metal contamination
8 removed in the SC1 step frequently originates as contamination in the
9 solutions utilized in the HF clean step (the above-described step 1C).
10 Additionally, a significant portion of the contaminants removed during the
11 SC2 step may originate from contaminated solutions utilized in the HF
12 clean step (the above-described step 1C) or from contaminated solutions
13 utilized in the SC1 step (the above-described step 1E). Accordingly, and
14 as part of the invention it is recognized that it may be possible to
15 eliminate one or both of the SC1 and SC2 steps of the RCA clean
16 process by reducing contamination introduced by, during or prior to the
17 HF clean step.

18 It should further be understood that the invention includes several
19 processes which may include one or more of the various process steps
20 described below, either alone or in combination with one or more of the
21 other of the process steps described below. Although not all combinations
22 may be fully appropriate or preferred, the various combinations of the
23 disclosed steps are contemplated as part of the implementation of the novel
24 concepts presented herein.

Processes Generally

Preferred methods according to several aspects of the present invention are discussed with reference to Fig. 2. The cleaning processes according to these first embodiments are most preferably illustrated as steps 2A-2D.

In one aspect the invention includes a first cleaning step, step 2A, which involves a first cleaning mixture or solution. The first cleaning mixture preferably includes at least one oxidizing agent as a constituent thereof. The first cleaning step removes contaminants, such as organic contaminants which are present on the surface. The first cleaning step can also include constituents which concurrently clean, dissolve or otherwise remove contaminants from the surface being treated. These actions can occur along with the preferred oxidizing action which both develops oxide on the surface of the semiconductor and tends to break up organics and other contaminants. The concurrent inclusion of other constituents, such as acids, can be used to remove contaminants such as metallic materials which sometimes plate or otherwise develop upon the surface of the semiconductor article. The first cleaning step is preferably performed by contacting a liquid upon the surface being treated, such as in a manner as described more fully below.

The cleaning processes in another aspect include a second step which is preferably a rinsing step. The preferred rinsing step helps to remove any materials which are oxidized, dissolved or otherwise removed from the surface in the first cleaning step. The rinsing step also serves to stop

1 or inhibit further chemical activity associated with the constituents included
2 in the first cleaning step. The second cleaning step is preferably
3 performed by rinsing a rinsing solution or other rinsing liquid against or
4 over the surface being treated.

5 The cleaning processes in another aspect preferably include drying
6 the surface to remove residual moisture or other materials remaining from
7 the prior cleaning and rinsing steps.

8 The cleaning processes in another aspect include removing oxide
9 from the surface. The removing is preferably accomplished by exposing
10 the surface to an oxide removal vapor. The oxide removal vapor includes
11 a suitable oxide removal agent, for example vaporous hydrogen fluoride or
12 a vapor mixture of hydrogen fluoride vapor and water vapor. Other
13 constituents can also be included in the oxide removal vapor used. The
14 oxide removal step is preferably accomplished without wetting the surface
15 so that a subsequent drying step of the resulting surface is not needed.
16 This is particularly of advantage when the surface being treated is left in
17 a hydrophobic condition as a result of the oxide removal step.

18 The steps explained above will now be described in greater detail
19 below. Alternative methods employing additional or alternative aspects of
20 the invention will also be described below.

21 22 First Cleaning Step

23 Referring to step 2A, a surface of one or more wafers or other
24 semiconductor articles are subjected to a first cleaning step. The first

1 cleaning step preferably uses a first cleaning fluid, which is advantageously
2 a mixture or solution containing primarily liquid constituents, but may also
3 include entrained or dissolved gases with the liquids. The first cleaning
4 step is performed to remove various contaminants from the surface being
5 treated. The preferred first cleaning step more specifically includes an
6 oxidizing action as at least part of the cleaning step. The oxidizing
7 action is preferably effected by contacting the surface or surfaces with a
8 first cleaning fluid which is advantageously an oxidizing solution that
9 includes an oxidizing agent or agents as at least one constituent thereof.

10 One preferred oxidizing agent is ozone. Ozone is preferably
11 introduced into the first cleaning solution in a variety of suitable ways.
12 One preferred way of introducing the ozone into such solution or other
13 fluid is to inject the ozone into a conduit through which a carrier or
14 other constituents of the first cleaning fluid is or are being supplied.
15 Another mode of using the ozone is to inject or bubble it into a tank
16 which contains the carrier chemical or chemicals which are chosen. The
17 ozone can go into solution or be partly entrained into the first cleaning
18 fluid.

19 When ozone is used, then the first cleaning fluid preferably includes
20 a carrier which can be relatively non-reactive, or can be itself a solvent,
21 an oxidizing agent, or other agent serving additional cleaning and treatment
22 purposes. One such carrier for ozone is water, more preferably deionized
23 water, or alternatively distilled water, or distilled and deionized water.
24 Other constituents of the first cleaning fluid also can be used and serve

1 as carriers of the ozone. The ozone can either be dissolved into the
2 liquid carrier or carriers, or it can be injected into a fluid supply stream
3 which causes portions of the ozone gas to dissolve thereinto and other
4 portions to be entrained into the fluid supply stream.

5 Ozone can also be introduced into the first cleaning fluid using a
6 carrier gas which facilitates handling of the ozone. Examples of suitable
7 carrier gases include oxygen, clean dry air, nitrogen, inert gases, and
8 potentially other gases which do not by chemical makeup lead to rapid
9 breakdown of ozone. The ozone is advantageously used in connection with
10 carrier gases such as oxygen, air or nitrogen in concentrations ranging
11 from about 1% to about 15% by weight relative to the other constituents
12 of the carrier gas stream.

13 The resulting ozone and carrier gas stream is introduced into the
14 first cleaning fluid in amounts sufficient to produce amounts of ozone in
15 the processing chamber and first cleaning fluid which are effective to
16 cause an oxidizing effect upon the surface being treated. For example
17 ozone and carrier gas introduced into a flowing first cleaning fluid stream
18 will advantageously be 1-10 liters per minute when injected into a first
19 cleaning fluid stream which is in the range from about 1 liter per minute
20 to about 10 liters per minute. Higher flows of the ozone carrier gas
21 mixture in the approximate range of 5-10 liters per minute are used when
22 injected with water or sulfuric acid. Whereas, lower flows of the ozone
23 carrier gas mixture in the approximate range of 2-5 liters per minute are
24 used when injected with water and hydrochloric acid.

1 The ozone can advantageously be used in deionized or other
2 appropriate water in amounts sufficient to produce concentrations by weight
3 of greater than about 0.001% ozone. More preferably, the ozone is
4 included in amounts sufficient to produce concentrations by weight in the
5 range from about 0.005% to about 0.01%. Such concentrations apply
6 whether the carrier includes a carrier gas, water alone, other liquid
7 constituents, or combinations thereof.

8 Other possible ozone carriers include acids, such as sulfuric acid
9 (H_2SO_4) or hydrogen chloride (HCl), such as in the form of hydrochloric
10 acid. The acids can potentially be used in concentrations ranging from
11 anhydrous acids, highly concentrated or varying dilutions thereof. For
12 example, concentrated sulfuric acid having approximately 96-98% sulfuric
13 acid with the remainder water is suitable. Other acids may be provided
14 in solutions of lower concentrations, such as aqueous solutions with water,
15 or possibly solutions formed with alternative solvents or other constituents
16 which also can serve as part of the carrier function or combined carrier
17 and cleaning fluid activities. For example, relatively less concentrations
18 of hydrochloric acid in the range of about 1-5% may be used. These or
19 other carriers used with ozone or other oxidizing agents can advantageously
20 also serve added cleaning functions.

21 Ozone can be used with acids, such as the hydrochloric or sulfuric
22 acids, in amounts sufficient to produce concentrations as recited above in
23 connection with use of ozone with a carrier comprising deionized water,
24 either alone or with other minor constituents.

One acid constituent used in some of the first cleaning liquids according to this invention is sulfuric acid. Sulfuric acid can be used in various concentrations ranging from approximately 1-100% by volume. More preferably, sulfuric acid is used in amounts which are complementary with the concentration of ozone, when ozone is used. If other ingredients are included, such as the hydrogen peroxide as explained below, then the sulfuric acid concentrations are reduced to accommodate the added constituents. A preferred sulfuric acid ozone mixture includes water in the amount of approximately 0-50% water, 0.001-0.01% ozone, and the balance being sulfuric acid and any other constituents.

Another suitable acid for use in the first cleaning fluid is hydrogen chloride in the preferred form of hydrochloric acid (HCl). The preferred concentration of hydrochloric acid differs from sulfuric acid. If other alternative acids are used, then concentrations will also typically vary dependent upon the acid selected and the particular types of contaminants being cleaned. When the acid selected is hydrochloric acid, then the preferred concentrations are from about 0.1% to about 10% HCl by weight, more preferably from about 0.5% to about 5% by weight. The remaining balance of the solution is in such cases are water, or more preferably a combination of water and ozone. When ozone is used, it is included in amounts sufficient to comprise the concentrations given above in connection with preferred ranges of ozone used in deionized water, or as more specifically indicated.

1 It should also be understood that the acids explained above can also
2 be used as part of the first cleaning solution without necessarily including
3 ozone mixed or in solution therewith. This is possible since the acid or
4 other constituent of the carrier can potentially serve to perform an
5 oxidizing function, or alternatively other oxidizing agents can be included
6 in the first cleaning liquid in addition to any acids used therein.

7 Another constituent which can be included in the first cleaning
8 solution is hydrogen peroxide (H_2O_2). Hydrogen peroxide serves as an
9 oxidizing agent and can be mixed with a suitable carrier. Hydrogen
10 peroxide is advantageously used with a carrier which acts as a diluent to
11 reduce the concentration thereof due to its highly reactive nature. Suitable
12 carriers include water or sulfuric acid, or combinations of water and
13 sulfuric acid. The preferred water and sulfuric acid ranges are given
14 above. The preferred ratios of hydrogen peroxide are from about 1% by
15 volume hydrogen peroxide to about 20% hydrogen peroxide, relative to the
16 carrier. In one embodiment the hydrogen peroxide is used in
17 concentrations sufficient to produce a volumetric ratio of about 1:10
18 (hydrogen peroxide:sulfuric acid).

19 The temperatures used in the first cleaning step will vary dependent
20 upon the constituency of the first cleaning liquid. In one preferred form
21 of the invention which utilizes sulfuric acid, the temperatures used are
22 elevated above room temperature and less than about 200°C, more
23 preferably the temperature range is from about 50°C to about 200°C, even
24

1 more preferably from about 75°C to about 150°C, still more preferably
2 from about 90°C to about 140°C.

3 In another form of the invention wherein hydrochloric acid is used
4 as a constituent of the first cleaning liquid, the temperatures are operated
5 in the range from about -5°C to about 25°C, more preferably from 0°C
6 to about 20°C, even more preferably from about 5°C to about 15°C.

7 The contacting of the first cleaning solution against the surface of
8 the wafer or other semiconductor article can be effected in several
9 different modes of operation. In one preferred mode of operation the
10 cleaning solution is sprayed against the wafers. This is advantageously
11 done within an enclosed processing chamber. It is also preferably done
12 while simultaneously rotating the wafer or batch of wafers so that the
13 spraying and contacting actions are done in a more uniform manner while
14 also performing a rotating action. The preferred rotational speeds and
15 volumetric flow rates are detailed below in connection with the description
16 of the second cleaning or rinsing step which also apply equally to the
17 first cleaning step, and such description will not be duplicated here.

18 When batches are being processed, then the wafers and any spray
19 nozzles are preferably arranged so that the first cleaning solution is
20 applied in an approximately uniform manner to all surfaces being treated.
21 Another possible mode of operation for the first cleaning step is to
22 provide the first cleaning solution in a tank or other container and to dip
23 or otherwise bring the wafer or other semiconductor article into contact
24 with the pool of cleaning liquid.

1 The amount of time needed to sufficiently complete the first cleaning
2 step will vary dependent upon the type of constituents included in the first
3 cleaning liquid, the type of article being processed, the prior processing
4 experiences of the surface being treated, and the temperature at which the
5 process is being performed. Other factors may also have some effect on
6 processing times. In general the processing times will range from about
7 30 seconds to about 20 minutes, more preferably from about 1 minute to
8 about 10 minutes.

9 10 **Second Cleaning Step - Using Rinsing Liquid**

11 Referring to step 2B, after the first cleaning step has been
12 performed, the wafers are preferably rinsed with a suitable second cleaning
13 liquid, such as a rinsing liquid. The rinsing liquid can advantageously be
14 formed primarily or totally from deionized or other suitable purified water.
15 Alternatively, other solvents, such as light alcohols or others, may also be
16 possible in addition or substitution to the use of water as the preferred
17 rinsing solvent.

18 The temperature of the rinsing or other second cleaning liquid is in
19 the range from about 5°C to about 100°C, more preferably from about
20 10°C to about 50°C, even more preferably from about 15°C to about
21 25°C.

22 The rinsing liquid can advantageously be sprayed upon the wafers
23 or other semiconductor surfaces in a manner similar to the first cleaning
24 liquid. In particular, the wafers or other semiconductor articles can

1 advantageously be spun at desirable rotational speeds while simultaneously
2 sprayed with water or other suitable rinsing liquids to dislodge any
3 residual first cleaning step liquid and particles, organics, metals or other
4 contaminants which may be on the surface or removed therefrom. The
5 spraying can be done initially without rotational action followed by
6 centrifugal action or intermittent centrifugal action to clear rinse liquid
7 from the surfaces being cleaned. Centrifugal action may also be desirable
8 for purposes of applying centrifugal forces which tend to dislodge
9 contaminants from the surface being cleaned. Suitable rotational speeds are
10 in the range from about 60 to about 3000 revolutions per minute, more
11 preferably from about 200 to about 2000 revolutions per minute, even
12 more preferably from about 300 to about 1500 revolutions per minute.

13 The volume of rinsing liquid used will depend on the number and
14 size of wafers or other articles being rinsed. For batches having about
15 twenty five silicon wafers of about 150 millimeters in diameter, a suitable
16 flow rate is in the range from about 1/2 gallon per minute to about 10
17 gallons per minute, more preferably from about 1 gallon per minute to
18 about 5 gallons per minute, even more preferably from about 2 to about
19 4 gallons per minute.

20 The preferred combined spray and centrifugal rinsing is
21 advantageously performed for a suitable period of time to remove most or
22 all of the residual first cleaning step liquid from the surface of the
23 semiconductor article. The spraying and spinning action can be performed
24 for a period from about 1 minute to about 20 minutes, more preferably

1 from about 2 minutes to about 10 minutes, even more preferably from
2 about 3 minutes to about 5 minutes.

3 Alternatively, the rinsing liquid can be applied against the surface
4 by immersing within a tank or reservoir of rinsing liquid using a variety
5 of techniques which are well-known in the art of semiconductor processing.
6 Rinsing times for immersion processing will typically be about one-half of
7 the times given immediate above with regard to spinning-spray processing.

8 9 Third Cleaning Step - Drying Surface

10 Referring to step 2C of Fig. 2, the wafers are preferably dried after
11 the rinsing step. The drying is primarily for the purpose of removing
12 any residual rinse liquid, such as rinse water, or to remove other
13 processing liquids which may otherwise be present from the first or second
14 cleaning steps. The drying is advantageously performed prior to removing
15 oxides using the oxide removal vapors described in greater detail below.
16 The drying step is significant in removing significant amounts of water or
17 other liquids which may cause the oxide removal step to progress at
18 varying rates and degrees of activity. The drying is also advantageously
19 performed prior to the oxide removal step in order to prevent the need
20 for significant drying after oxide is removed. The removal of oxide can
21 leave the surface hydrophobic or otherwise more susceptible to particle
22 attachment or other adherence from contaminants which become deposited
23 thereon. Such a surface tends to cause adherence in a manner which
24 renders the contaminants difficult to remove.

1 The drying step is advantageously accomplished by passing a flow
2 of clean dry air, nitrogen, inert gases, or other suitable drying gases over
3 the surfaces being dried. The use of nitrogen is advantageous due to
4 relatively easy availability and well-established techniques for rendering the
5 surfaces clean and dry.

6 The volumes of drying gas and temperatures used can vary
7 considerably. Increased flow rates and higher temperatures tend to
8 decrease drying times. Typical volumetric rates for a centrifugal batch
9 processor as explained above are in the range from about 1 to about 100
10 liters per minute. Temperatures will typically be in the range from about
11 15°C to about 100°C. Associated drying time will typically range from
12 about 2 minutes to about 20 minutes, more preferably from about 4
13 minutes to about 10 minutes.

14 The drying action can be done without centrifugal action, or more
15 preferably is done simultaneously with centrifugal action to help clear rinse
16 liquid from the surfaces and minimize drying times. Rotational speeds
17 similar to those set out above apply to any rotation employed during the
18 drying step.

19 Other drying techniques may alternatively be employed such as
20 condensing an organic film to displace water and then drying the organic
21 material from the surface. An example organic film is isopropyl alcohol.
22
23
24

Fourth Cleaning Step - Removing Oxide from Surface

Referring to step 2D, the surfaces being cleaned are also preferably subjected to an oxide removal step as part of the cleaning process. The oxide removal process helps to remove any particles or other contaminants which may be embedded within, adsorbed or absorbed upon, or otherwise adhered to the oxide layer present upon the surface of the wafer or other semiconductor article being cleaned. The oxide removal process utilizes an oxide removal agent which is preferably presented as a gas or other vapor as compared to treatment as a liquid. Treatment with a vapor eliminates the need for a subsequent drying step. Treatment with a vapor also minimizes the risk of imparting various metallic contaminants which may be easily picked up by the oxide removal agents if employed in a liquid form. Vapor processing has also been found advantageous as part of the invention since even if some metallic or other contaminants may be present in the liquid source materials, the use of vapors generated from the liquid source materials tends to provide a purer processing fluid than if liquid is employed. This may be true since heavier contaminants will tend to stay in the liquid phase as distinct from the vapors which are generated therefrom.

The use of hydrogen halide vapor in step 2D can reduce or eliminate previous metallic contamination of wafers which occurred during the above-discussed use of hydrogen halide solution in 1C of the RCA process. Specifically, many contaminants, particularly metallic contaminants, remain primarily in a solution as hydrogen halide vapors are

1 generated from the solution. Hydrogen halide vapors are therefore
2 generally a preferred source of hydrogen halide than are hydrogen halide
3 solutions in liquid form.

4 Preferred oxide removal agents include hydrogen halides which are
5 preferably provided in the indicated vapor form. One preferred hydrogen
6 halide is hydrogen fluoride. Other hydrogen halides may also be useful
7 depending upon the type of semiconductor oxide being removed. Hydrogen
8 fluoride is a preferred hydrogen halide for use in step 2D due to its high
9 effectiveness in removing silicon oxides, and in part because of its
10 relatively high volatility compared to other hydrogen halides. However,
11 other hydrogen halides, in addition to or in substitution for hydrogen
12 fluoride, may provide specific advantages for step 2D. For instance,
13 hydrogen chloride would have the advantages that a significant amount of
14 hydrogen chloride is typically already present at semiconductor processing
15 sites, as hydrogen chloride is typically used in such sites for removal of
16 metals during semiconductor wafer processing. Accordingly, in certain
17 applications it may be desirable to replace the generally preferred hydrogen
18 fluoride vapor in whole or in part with hydrogen chloride vapor.

19 Hydrogen fluoride or other oxide removal vapors can be generated
20 by using a liquid mixture or solution comprising the active oxide removal
21 agent, such as hydrogen fluoride, and a diluent. Suitable diluents include
22 water and isopropyl alcohol, or mixtures of water and isopropyl alcohol.
23 The active hydrogen fluoride and/or other oxide removal agents are
24 included in sufficient vapor concentrations to provide desirable oxide

1 removal rates. In the case of hydrogen fluoride (HF), the vapor mixtures
2 generated from either HF diluted with water or isopropyl alcohol or
3 mixtures thereof are generally in the range from about 1:10,000 to about
4 1:1 (HF:diluents), more preferably from about 1:1000 to about 1:1, even
5 more preferably from about 1:100 to about 1:1, for example 1:10-1:1.

6 The vaporous hydrogen halides or other oxide removal agent or
7 agents can be communicated to the surface of the wafer using a suitable
8 carrier gas. Examples of suitable carrier gases include clean dry air,
9 nitrogen, and inert gases. The amount of carrier gas used will vary the
10 vapor concentration of the active oxide removal agent. In many situations
11 the diluent carrier gas will comprise from about 1:500 to about 1:5000
12 (active vapors:diluent carrier gas).

13 In many of the preferred processes according to this invention the
14 vapors are generated from liquid source materials by passing a carrier or
15 feed gas thereover or therethrough. Due to the dilution brought about by
16 the carrier gas, the preferred concentrations of liquid constituents used in
17 the liquid source materials will typically be more concentrated than the
18 desired vapor concentrations developed in the processing chamber. For
19 example when HF is used with water or isopropyl alcohol, the liquid
20 proportions will generally be in the range from about 1:1,000 to about
21 1,000:1 (liquid HF:liquid diluents), more preferably from about 1:100 to
22 about 100:1, even more preferably from about 1:10 to about 10:1, for
23 example 1:1.

1 It has been found experimentally that in the absence of isopropyl
2 alcohol, a hydrogen fluoride vapor treatment works better when run in a
3 natural polyethylene chamber, than when run in a tetrafluoroethylene
4 (PTFE) Teflon chamber. This may be due to the porosity and amount of
5 absorbed moisture in the PTFE chamber contributing to instability of the
6 hydrogen fluoride treatment process.

7 By utilizing the novel processes described herein, including the
8 relatively pure hydrogen halide vapors instead of the prior art use of
9 liquid hydrogen halide liquid solutions, it is possible to eliminate one or
10 more steps from the prior art cleaning processes commonly referred to as
11 the RCA cleaning processes. For instance, by utilizing hydrogen fluoride
12 vapor in step 2D it is possible to eliminate steps 1E-1I of the prior art
13 RCA clean process. (Compare, Fig. 1 prior art RCA process with the
14 Fig. 2 embodiment of the present invention.)
15

16 **Alternative Oxide Removal Step**

17 In other aspects of the Fig. 2 embodiment, step 2D may comprise
18 treatment with a mixture of hydrogen halide vapor and ozone. Most
19 preferably, the hydrogen halide vapor will be hydrogen fluoride vapor.
20 Such simultaneous treatment with ozone and hydrogen fluoride vapor
21 believed to create a continuous etch-oxidation cycle wherein the ozone
22 performs by generating oxide film, and the oxide removal agent performs
23 by concurrently removing the oxide film. This continuous etch-oxidation
24 removal cycle may be particularly advantageous in applications wherein one

1 or two microns of material is to be removed from a silicon-comprising
2 wafer, such as in a stress relief etch. Also, such treatment may be
3 advantageous for removal of several angstroms of silicon-comprising
4 material, such as when it is necessary to remove material from exposed
5 surfaces prior to metal deposition to insure good ohmic contacts.

6 It is noted that in applications utilizing a mixture of ozone and
7 hydrogen halide vapors, it is most preferable to exclude isopropyl alcohol
8 and other organic vapors from the vapor mixture to reduce the risk of
9 uncontrolled reactions, such as fire and/or explosion. It is also
10 advantageous to exclude organic liquids or vapors which may result
11 therefrom with regard to the previous rinsing and drying steps.

12 Ozone generation is preferably from diatomic oxygen and can be
13 accompanied by mixtures of nitrogen and carbon dioxide gases which also
14 serve to form a blended carrier gas for the ozone. Ozone concentrations
15 in the gas stream are typically in the range from about 1% to about 10%
16 by weight. Flow rates are typically from about 1 liter per minute to
17 about 15 liters per minute.

18 The ozone containing gas stream can advantageously be used as a
19 feed gas to a vapor generator which generates vapors of HF.
20 Alternatively, the ozone bearing gas stream can be independently introduced
21 into a processing chamber, or more preferably, blended into a vapor
22 stream bearing the HF and other constituents carrying the etching or oxide
23 removal vapor to the processing chamber.
24

1 The specific mixture of ozone and oxide removal vapors can be
2 constituted to control the rate of silicon oxidation and the concurrent rate
3 of oxide removal. The resulting net rate of change in the oxide layer
4 thickness can accordingly be controlled. The simultaneous oxide removal
5 and oxide growth causes sub-layers of oxide to be exposed and removal
6 of particles is thereby facilitated.

7 8 Second Alternative Oxide Removal Step

9 Other alternative processes according to the invention include adding
10 addition vapor streams to the active oxide removal agent and diluent
11 solvent or solvents used therewith as described herein. In particular it is
12 believed that vapor mixtures of hydrogen halide oxide removal agents, such
13 as HF, diluted with isopropyl alcohol and water are suitable for
14 combination with additional vapor streams. Example additional vapor
15 streams include metals solubilizing agents, such as a hydrogen halide or
16 mixture of hydrogen halides, in particular hydrogen chloride, preferably in
17 the form of diluted hydrochloric acid vapors. Exemplary concentrations
18 are in the preferred ranges given above in connection with the hydrogen
19 fluoride vapor concentrations and such apply to both the HF component
20 and the supplemental secondary or additional mixed components. Other
21 metals solubilizing acids may also be suitable for inclusion in the vapor
22 phase oxide removal step.

23 The combination of vapors for both oxide removal and metals
24 solubilization may have synergistic effects in which improved wafer

processing is achieved. Although the mechanism may or may not be fully understood, it is hypothesized that the strong inter-molecular forces are developed between metallic fluorides and more volatile components of the vapor stream, such as HF and water which are highly polar molecules that can form hydrogen bonds with metallic fluorides which may be formed.

It is possible to mix various aqueous hydrogen halide solution in a single vapor generator. However, control of such mixtures can become difficult due to differing vapor pressures of the constituent hydrogen halides or other mixed constituents. Therefore, it may be desirable to separately generate the various vapors and then mix the resulting vapor streams in a feed line or in the processing chamber itself. The preferred hydrogen halide vapors can advantageously be generated from aqueous mixtures of each hydrogen halide in separate vapor generators and then the streams are mixed using precise control of the flow rate of each vapor stream. Most preferably, an inert carrier, such as nitrogen gas is passed through the vapor generators. The flow rate of the carrier may vary from about 1 to about 60 liters per minute. The vapor generators are advantageously kept in the temperature range from about 10° to about 30°C, more preferably from about 20° to about 25°C. When the mixture is a preferred mixture containing HF and HCl, the HF concentration can range from about 1% to about 50% by weight, and HCl concentrations can range from about 1% to about 30% by weight. These vapor streams can be mixed with an organic vapor stream, such as isopropyl alcohol, or isopropyl alcohol can be included in the liquid mixture from which one

1 or both of the hydrogen halides are preferably individually vaporized.
2 Additional aspects of mixed acid vapors are explained in my prior U.S.
3 Patent No. 5,232,511 which is incorporated by reference in its entirety.
4

5 **Alternative Embodiment Cleaning Processes**

6 Further embodiments of preferred methods according to the present
7 invention are illustrated in Fig. 3. These methods bear similarity to the
8 methods described hereinabove with variations therefrom as specifically
9 described below. Fig. 3 show that these embodiments comprise steps 3A-
10 3C.

11 Referring to step 3A, one or more semiconductor wafers or other
12 semiconductor articles being cleaned are exposed to a first cleaning step
13 which comprises water and ozone. The water and ozone are as described
14 above. Other chemical constituents are typically limited or eliminated so
15 as to reduce, or more preferably, eliminate the need for a rinsing step as
16 described above. The ozone performs the oxidization agent function and
17 the simultaneous use of the carrier liquid in the form of purified water
18 functions to rinse the surfaces to reduce or eliminate contaminants present
19 thereon. Additional rinsing is expected to not be needed. Processing
20 steps are otherwise as described above in connection with the processes in
21 connection with Fig. 2.
22
23
24

Further Alternative Embodiment Methods

The embodiments of Figs. 2 and 3 eliminate the SC1 step (step 1F) of the typical prior art RCA clean. Such removal of the SC1 step may be disadvantageous in certain applications, as the SC1 clean is currently one of the better methods known for removing particles from a silicon wafer. For instance, wafers containing a high amount of particles (which are most wafers after they have been subjected to processing, as such wafers typically comprise deposited photoresist or other organic materials upon them) may be difficult to clean without a particle removing SC1-type step. Therefore, a hybrid method of the invention is proposed to incorporate the SC1 step after the first cleaning step and second cleaning step. The SC1 step would be followed by a rinsing step similar to the second cleaning step described above. Thereafter the drying and vapor processing steps described above would be employed. Preferred concentrations for the water, hydrogen peroxide, and ammonium hydroxide constituents of the preferred SC1 step range between about 100:10:1 (water:hydrogen peroxide:ammonium hydroxide) to about 5:2:1.

The above discussed embodiments are thought to offer a process by which a hydrophobic surface may be formed on a semiconductor surface, such as a silicon-comprising wafer, by developing an oxide followed by etching or removing the developed oxide film without depositing metals or particles. Additionally, since the wafers are never wetted in a hydrophobic state, advanced drying technologies are not necessary.

1 **Example 1**

2 Silicon wafers having a diameter of approximately 150 millimeters
3 where intentionally contaminated by immersion in a high pH solution (pH
4 approximately 9-10) containing aluminum and iron ions. Such ions tend
5 to plate onto silicon surfaces in such high pH environments. Control
6 wafers were left unprocessed and the results are shown in the following
7 Table 1.

8 Standard cleaning procedure wafers were processed according to prior
9 art techniques using a process similar to Fig. 1 using the following
10 process parameters. Processing was conducted in a centrifugal spray acid
11 processor produced by Semitool, Inc. of Kalispell MT, Model SAT. The
12 centrifugal spray acid processor can be adapted to include mixing features
13 as ~~explained in the copending U.S. Patent Application Serial No.~~
14 ~~08/607,627 filed February 26, 1996 which is hereby incorporated~~ hereinto
15 in its entirety to provide explanation of exemplary systems used to mix
16 gaseous phase carriers and vapors generated from liquids. Such application
17 is attached hereto as an Appendix for convenience.

18 The piranha clean, step 1A, utilized 10 parts sulfuric acid (~96%)
19 to 1 part hydrogen peroxide. The piranha clean was conducted at
20 approximately 130°C for a period of 5 minutes at rotational speeds of
21 approximate 100 revolutions per minute. Step 1B was done using room
22 temperature deionized water for about 3 minutes at 2 gallons per minute
23 in the centrifugal spray processor at similar rotational speeds to step 1A.
24 Step 1C was conducted using 100:1 (water:HF) which was sprayed for 30

seconds onto wafers rotating at similar speeds. Step 1D rinsing was conducted similar to step 1B.

Step 1E utilized 5:1:0.25 (water:hydrogen peroxide:ammonium hydroxide) at room temperature for a period of 5 minutes and at rotational speeds similar to step 1A. Rinsing step 1F was similar to step 1B. Step 1G utilized 5:1:1 (water:hydrogen peroxide:hydrogen chloride) at room temperature for a period of 90 seconds and at rotational speeds similar to step 1A. The results for the standard clean are shown in the following Table 1.

Table 1 also shows results for a Cleaning Process A which involved the following processing parameters. In conjunction with step 2A, ozone was injected into a first cleaning mixture of sulfuric acid (~96%) and hydrogen peroxide in ratios of 10:1 (sulfuric acid:hydrogen peroxide). The cleaning mixture was at elevated temperatures in the range of approximately 90°C. The ozone was provided in a carrier gas of oxygen with combined flow rate of 10 liters per minute, the ozone making up approximately 8% by weight of the flowing gas stream. Rotational speeds were as described relative to step 1A. Flow rate of the first cleaning mixture was approximately 20 liters per minute sprayed onto the rotating wafers for a period of about 5 minutes. Step 2B involved spraying deionized water in a manner similar to the description of step 1B. The drying step 2C was performed using nitrogen in manner similar to step 1E.

1 Step 2D was performed for a period of about 5 minutes using a
2 vapor mixture of HF and isopropyl alcohol generated using a ratio of
3 liquids equal to 1:100 (HF:isopropyl alcohol) at room temperatures (20°C).
4 The oxide removal step was targeted to remove about 50 angstroms
5 thickness of silicon oxides.

6 Table 1 further shows results for a Cleaning Process B which was
7 performed in the following manner. The first cleaning mixture included
8 hydrogen chloride (HCl) supplied in the form of a 37% solution thereof
9 in water. Such a 37% solution of HCl was included in amounts sufficient
10 to provide a concentration thereof equal to 2% by volume with water.
11 Ozone was also included in solution therewith. Ozone and carrier gas
12 oxygen were injected into the flowing stream of cleaning liquid at a flow
13 rate of about 7 liters per minute, with ozone making about 8% by weight
14 of the flowing gas stream.

15 The rinsing, drying and oxide removal steps 2B, 2C and 2D were
16 similar to those described above in connection with the Cleaning
17 Process A.

18 The results shown in Table 1 indicate approximate metals
19 concentrations on the cleaned surface using vapor phase decomposition ion-
20 coupled plasma mass spectrometry. The performance of the Cleaning
21 Process A and Cleaning Process B are superior with respect to some of
22 the metals analyzed and less effective with regard to other metals. In
23 almost all cases the performance was either better or sufficiently similar
24

to performance demonstrated by the RCA clean described above so as to be a commercially viable alternative thereto.

TABLE 1

Sample Type	10^{10} Atoms/cm ²						
	Na	Al	Cr	Fe	Ni	Cu	Zn
Control	14	2300	0.4	650	0.2	1.3	10
Standard clean	2.4	13	<0.1	<0.6	<0.1	0.1	<0.5
Cleaning Process "A"	18	9.8	<0.1	<0.6	<0.1	0.1	0.5
Cleaning Process "B"	1.6	120	<0.1	4.6	<0.1	<0.1	<0.5

Example 2

Table 2 shows processes as described in connection with Example 1 conducted upon wafers which were intentionally contaminated by immersion in an aqueous solution containing a small amount of n-methyl pyrrolidone. The wafers were processed through the respective cleaning or control regimes and then analyzed using X-ray phosphorescence spectroscopy to evaluate the residual carbon and other results indicated.

TABLE 2

Sample Type	Atomic Concentration (%)						
	C	O	N	F	Si	% element -al Si	% oxide Si
Control	2.7	33.2	-	0.3	63.9	90	10
Standard Clean	2.3	29.5	0.1	0.3	67.9	89	11
Cleaning Process A	1.7	4.4	0.1	0.9	92.7	100	0
Cleaning Process B	1.6	4.4	-	0.8	93.2	100	0

Example 3

Table 3 shows processes as described in connection with Example 1 conducted upon wafers which were intentionally contaminated by immersion in an aqueous solution containing a small amount of ethylene glycol. The wafers were processed through the respective cleaning or control regimes and then analyzed using X-ray phosphorescence spectroscopy to evaluate the residual carbon and other results indicated.

TABLE 3

Sample Type	Atomic Concentration (%)						
	C	O	N	F	Si	% element -al Si	% oxide Si
Control	23.3	33.2	-	0.3	63.9	90	10
Standard Clean	4.7	30.0	0.1	0.4	64.8	89	11
Cleaning Process A	2.2	4.1	0.1	0.9	92.7	100	0
Cleaning Process B	1.9	4.2	-	0.9	93.0	100	0

Example 4

Virgin silicon wafers were processed using processes as described in connection with Example 1. This was done to indicate the amount of metals contamination which might be associated with the various cleaning processes themselves. Analysis was performed using vapor phase decomposition ion-coupled plasma mass spectrometry. The results are shown in Table 4.

TABLE 4

Sample Type	10^{10} Atoms/cm ²						
	Na	Al	Cr	Fe	Ni	Cu	Zn
Control	12	0.8	1.4	5.1	0.7	0.1	<0.5
Standard Clean	9.2	13	<0.1	<0.6	<0.1	<0.1	0.6
Cleaning Process A	16	<0.5	<0.1	<0.6	<0.1	0.2	0.5
Cleaning Process B	2.6	<0.5	<0.1	<0.6	<0.1	0.4	<0.5

Example 5

Wafers can be processed using a deionized water ozone mixture. Ozone is injected as a gas stream having a concentration of ozone in nitrogen, clean dry air, or other carrier gas which is preferably in the range of 5-15% ozone by volume in the gas stream, more preferably 7-10% ozone. The deionized water ozone and carrier gas mixture is sprayed against the wafers in step 3A for a period of time sufficient to produce the desired degree of oxidation and breakup of surface contamination. Appropriate times are believe to be approximately 10-20 minutes. Rotation advantageously occurs at the same rotational speeds as indicated for step 1B, explained above. Temperatures in the range of 50-90°C are advantageously used.

1 Steps 3B and 3C are performed as indicated above with regard to
2 steps 2C and 2D.

3 4 **Example 6**

5 Silicon wafers can be processed using a process similar to that
6 described in Example 1 with regard to steps 2A, 2B, and 2C. Step 2D
7 can be performed using a mixture of ozone and HF vapor generated using
8 a feed gas stream having an approximate ozone concentration of 8% by
9 weight of the feed gas. This feed gas is passed through a vapor
10 generator at a rate of about 8 liters per minute. The vapor generator
11 contains a liquid mixture of water and HF which is 5% by weight HF.
12 Net oxide removal rates of 20 angstroms per minute are expected. The
13 rate of oxide removal can be adjusted by feeding into the processing
14 chamber a second vapor stream generated in a second vapor generator
15 which produces water vapor.

16
17 In compliance with the statute, the invention has been described in
18 language more or less specific as to structural and methodical features.
19 It is to be understood, however, that the invention is not limited to the
20 specific features shown and described, since the means herein disclosed
21 comprise preferred forms of putting the invention into effect. The
22 invention is, therefore, claimed in any of its forms or modifications within
23 the proper scope of the appended claims appropriately interpreted in
24 accordance with the doctrine of equivalents.